



TITLE:

Isotopic constraints on biogeochemical cycling of copper in the ocean.

AUTHOR(S):

Takano, Shotaro; Tanimizu, Masaharu; Hirata, Takafumi; Sohrin, Yoshiki

CITATION:

Takano, Shotaro ...[et al]. Isotopic constraints on biogeochemical cycling of copper in the ocean.. Nature communications 2014, 5: 5663.

ISSUE DATE:

2014-12-05

URL:

<http://hdl.handle.net/2433/192254>

RIGHT:

© 2014 Macmillan Publishers Limited.; 許諾条件により本文は2015-06-06に公開.; この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。; This is not the published version. Please cite only the published version.

1 Isotopic Constraints on Biogeochemical Cycling of Copper in the Ocean

2

3 Shotaro Takano^{1*}, Masaharu Tanimizu², Takafumi Hirata³, and Yoshiki Sohrin¹

4 ¹*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

5 ²*Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and*

6 *Technology, 200 Monobe Otsu, Nankoku 783-8502, Japan*

7 ³*Laboratory for Planetary Sciences, Division of Earth and Planetary Sciences, Kyoto*

8 *University, Kitashirakawa Oiwake-cho, Kyoto 606-8502, Japan*

9 ***Corresponding author.** E-mail: shotaro@inter3.kuicr.kyoto-u.ac.jp Tel: +81 774 38

10 3098. Fax: +81 774 38 3099

11

Trace elements and their isotopes are being actively studied as powerful tracers in the modern ocean and as proxies for the palaeocean. Although distributions and fractionations have been reported for stable isotopes of dissolved Fe, Cu, Zn, and Cd in the ocean, the data remain limited and only preliminary explanations have been given. Copper is of great interest because it is either essential or toxic to organisms and because its distribution reflects both biological recycling and scavenging. Here, we present new data of isotopic compositions of dissolved Cu ($\delta^{65}\text{Cu}$) in seawater and rainwater. The Cu isotopic composition in surface seawater is explained by the mixing of rain, river, and deep water. In deep seawater, $\delta^{65}\text{Cu}$ becomes heavier along oceanic circulation because of preferential scavenging of the lighter isotope (^{63}Cu). Additionally, we constrain the marine biogeochemical cycling of Cu using a new box model based on Cu concentration and $\delta^{65}\text{Cu}$.

Copper plays an important role as a micronutrient for organisms in the ocean, but high concentrations of the free Cu^{2+} ion are toxic¹. Dissolved Cu has concentrations of 0.5–6 nmol kg⁻¹ in seawater and mostly complexes with organic ligands, which results in very low concentrations (fmol kg⁻¹ to pmol kg⁻¹) of the free Cu^{2+} ion².

30 Vertical distributions of dissolved Cu are of the nutrient-scavenging hybrid type³.
31 Generally, the concentrations of nutrient-type trace metals (e.g., Zn, Ni, and Cd) are low
32 in the surface layer of the ocean because of biological uptake. However, the
33 concentrations increase with depth, showing a mid-depth maximum because of
34 remineralisation from settling particles. By contrast, the concentration of dissolved Cu
35 gradually increases with depth towards the bottom. Such distributions have been
36 interpreted to be caused by a combination of scavenging throughout the water column
37 and a supply from the uppermost layer of benthic sediments, where scavenged Cu is
38 recycled to overlying seawater via early diagenesis^{4,5}. Copper has two stable isotopes,
39 ⁶³Cu and ⁶⁵Cu, and its isotopic composition is reported as $\delta^{65}\text{Cu}(\text{‰}) =$
40 $[(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}/(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST SRM 976}} - 1] \times 10^3$. To date, only a few vertical profiles of
41 dissolved $\delta^{65}\text{Cu}$ in the ocean have been reported^{6, 7, 8, 9}. The reported $\delta^{65}\text{Cu}$ values
42 (0.44–1.44‰) were substantially heavier than typical values for the solid Earth (~0‰)¹⁰.
43 ¹¹. However, as there were relatively large uncertainties in the reported data, it has been
44 difficult to elucidate intra-ocean distributions. This is partly due to analytical difficulties
45 in the determination of $\delta^{65}\text{Cu}$ caused by the interference of matrices and the
46 inapplicability of the so-called double-spike technique.

47 Recently, we developed a simple and precise analytical method for $\delta^{65}\text{Cu}$ based

on a chelating resin extraction technique¹². Here, we use this method to present new data of isotopic compositions of dissolved Cu ($\delta^{65}\text{Cu}$) in seawater from the North/South Atlantic, South Indian, and North Pacific. We also present new data of rainwater samples collected from urban and rural regions. Using these data, the Cu isotopic composition in surface seawater is explained in an oceanographic context. In deep seawater, $\delta^{65}\text{Cu}$ values show a liner correlation with apparent oxygen utilisation (AOU), which suggests $\delta^{65}\text{Cu}$ becomes heavier along oceanic circulation because of preferential scavenging of the lighter isotope (i.e., ^{63}Cu). These are the first data showing that the stable isotopic composition of trace metals changes systematically with the age of deep water. Additionally, we propose a new box model for Cu in the ocean based on the combination of Cu concentration and $\delta^{65}\text{Cu}$, which successfully constrains the marine biological cycling of Cu.

Results

Seawater analyses

The observed oceanic stations are shown in Fig. 1. All seawater data are summarised in Supplementary Table 1. The vertical profiles of dissolved Cu concentration and $\delta^{65}\text{Cu}$ for each station are presented in Supplementary Fig. 1, and

representative profiles are shown in Fig. 2. The Cu concentrations were in the range of 0.6–4.6 nmol kg⁻¹, and the profile at station ER10 agreed well with that determined in separate samples collected at the same station in our previous research (Supplementary Fig. 2)¹⁴. The $\delta^{65}\text{Cu}$ values ranged from +0.41‰ to +0.85‰, which were smaller than values determined by a Mg(OH)₂ co-precipitation technique (+0.50–1.44‰)^{7, 8} at other stations and similar to values determined by a solvent extraction technique (+0.44–0.78‰)^{6, 9} at other stations (Supplementary Fig. 3). The vertical samples from BATS have been analysed using a solvent extraction technique by Thompson et al.⁹. The reported $\delta^{65}\text{Cu}$ value (0.56±0.09‰) for a 2000 m depth sample was higher than our value (0.41±0.05‰). Unfortunately, we are not able to investigate the causes because the BATS samples have been exhausted. Recently, we performed intercalibration of $\delta^{65}\text{Cu}$ with a group from ETH, Zurich (see Acknowledgements section for details) using seawater collected at a station near the Japan Trench, of which the details are described in Supplementary Methods. The ETH group used a new method based on Al(OH)₃ co-precipitation¹⁵, which gave results consistent to ours (Supplementary Fig. 4).

The vertical profiles of $\delta^{65}\text{Cu}$ in this work showed a common feature: $\delta^{65}\text{Cu}$ was ~0.5‰ in the surface layer and became heavier at depth. Station BD21 above the Juan de Fuca Ridge had a minimum Cu concentration at a depth of 2300 m, reflecting

the effect of a hydrothermal plume¹⁶. There were, however, no significant variations in $\delta^{65}\text{Cu}$.

Rainwater analyses

We also determined $\delta^{65}\text{Cu}$ in rainwater for the first time (Table 1). Rainwater was sampled from rural and urban regions in Japan. The dissolved $\delta^{65}\text{Cu}$ values were in the narrow range of -0.12 – $+0.03\text{‰}$ and did not show significant differences depending on location and time, whereas the Cu concentrations varied largely (1.1 – $23.5 \text{ nmol kg}^{-1}$), which may reflect various contributions of anthropogenic input. It has been reported that $\delta^{65}\text{Cu}$ values were $\sim 0 \text{ ‰}$ for leachable fractions of marine aerosols¹¹ and bulk loess¹⁷. Rainwater would scavenge both atmospheric dusts and anthropogenic aerosols during precipitation. Therefore, it seems reasonable to presume the $\delta^{65}\text{Cu}$ value for atmospheric input to be zero.

Copper isotopes in surface seawater

In Fig. 3, the $\delta^{65}\text{Cu}$ in surface seawater is plotted against the reciprocal Cu concentration together with the ranges and averages of deep seawater, rural rainwater, and river water⁸. Assuming that average surface seawater is a mixture of average rural

rainwater, average river water, and average deep seawater, the plot would be located in the magenta triangle. Evaporation that is another important factor to control salinity; it would increase the Cu concentration but not change the $\delta^{65}\text{Cu}$. However, the surface water data are shifted to the right of the triangles, indicating there must be other processes that decrease the dissolved Cu concentration (up to one tenths) while keeping the $\delta^{65}\text{Cu}$ values constant. The most likely process is phytoplankton uptake and adsorption of Cu onto the phytoplankton surface. It is well known that these processes produce biogenic sinking particles in the surface layer and they transport trace metals to the deep layer. Our data suggest that uptake and adsorption by phytoplankton in the open ocean does not cause significant fractionation of Cu isotopes. To clarify mechanisms controlling the Cu concentration and $\delta^{65}\text{Cu}$, it is informative to compare Cu and Cd in the ocean. For vertical profiles of dissolved Cd, the isotopic ratio ($\epsilon^{114}\text{Cd}$) correspondingly increases with a decrease in the concentration in the surface layer and decreases with an increase in the concentration from the surface to the intermediate layer, because biological uptake causes isotopic fractionation of Cd^{18, 19, 20}. Therefore, the profile of $\epsilon^{114}\text{Cd}$ from the surface to the intermediate layer becomes a mirror image of the concentration, and $\epsilon^{114}\text{Cd}$ linearly correlates with the logarithm concentration in the surface layer because of Rayleigh fractionation during biological uptake^{18, 19, 20, 21}.

However, $\delta^{65}\text{Cu}$ does not change uniformly with respect to the Cu concentration from the surface to the intermediate layer (Fig. 2 and Supplementary Fig. 1), and does not correlate with the logarithmic concentration in the surface layer (Supplementary Fig. 5). These facts also indicate biological processes cause insignificant fractionation of the Cu isotopes.

Copper isotopes in deep seawater

Given that uptake and adsorption of Cu by phytoplankton does not cause fractionation of Cu isotopes, biogenic sinking particles would have the same $\delta^{65}\text{Cu}$ value as surface seawater. Copper regenerated through decomposition of the biogenic sinking particles should produce $\delta^{65}\text{Cu}$ values in deep seawater, which are the same as those in surface seawater under this assumption. However, observed $\delta^{65}\text{Cu}$ in deep seawater is heavier than that in surface seawater. In addition, the profiles of $\delta^{65}\text{Cu}$ are similar to those of apparent oxygen utilisation (AOU; Fig. 2 and Supplementary Fig. 1). All $\delta^{65}\text{Cu}$ values are plotted against AOU, revealing a positive correlation ($R^2 = 0.60$, $n = 77$; Fig. 4a). In the layer deeper than 2000 m, $\delta^{65}\text{Cu}$ vs. AOU shows a stronger correlation ($R^2 = 0.70$, $n = 25$; Fig. 4b). Because AOU is a measure of the age of deep water, these data imply that $\delta^{65}\text{Cu}$ increases through deep water circulation. When the

138 Cu concentration is plotted against AOU, there is also a weak correlation ($R^2 = 0.31$, $n =$
139 77, Fig. 5).

140 In the case of Cd, the dissolved concentration is very low ($\sim 0.001 \text{ nmol kg}^{-1}$) in
141 the surface layer because of biological uptake, and it is high in the deep layer ($\sim 1 \text{ nmol}$
142 kg^{-1}) because of remineralisation from biogenic particles; it also increases along the
143 global deep circulation³. Because there is a significant correlation between Cd and
144 phosphate, the distribution of Cd is dominated by biogeochemical recycling. The
145 isotopic composition of Cd is heavier in surface seawater ($\epsilon^{114/110}\text{Cd} = 10\text{--}40$ with
146 respect to a JMC Cd Münster solution) than in deep seawater ($\epsilon^{114/110}\text{Cd} = \sim 3$) that is
147 almost uniform in the world ocean^{18, 19, 20}. Biological uptake depletes the Cd
148 concentration and preferentially leaves isotopically heavy Cd in surface seawater. It is
149 suggested that Cd in a replenished surface seawater reservoir is originally characterised
150 by $\epsilon^{114/110}\text{Cd} = \sim 3$ and that this Cd is almost quantitatively transported by biogenic
151 sinking particles from the surface to depth and remineralised in deep water; thus, the Cd
152 isotopic composition of deep water is homogeneous, whereas the Cd concentration
153 increases along with deep water circulation.

154 The $\delta^{65}\text{Cu}$ in deep seawater appears to be controlled by a ubiquitous effect
155 throughout the water column and deep water pathway because $\delta^{65}\text{Cu}$ correlates with

AOU. Copper is more strongly scavenged than other recycled-type trace metals such as Cd^{3, 5}. The scavenging is likely the reason that $\delta^{65}\text{Cu}$ is heavy in the deep layer and becomes heavier with the age of deep seawater. If this is true, ^{63}Cu would be preferentially adsorbed to sinking particles and preserved in sinks. The low linearity of Cu concentration against AOU (Fig. 5) would be due to the combination of scavenging throughout the water column and supply from sediments through decomposition of the organic fraction of sinking particles. The Cu released from sediments most likely has a $\delta^{65}\text{Cu}$ value similar to that in seawater near the bottom, resulting in the linearity of $\delta^{65}\text{Cu}$ vs. AOU.

Box model for Cu in the modern ocean

We present a new box model for Cu based on both concentration and isotopic composition (Fig. 6 and Supplementary Table 2). This model assumes a steady-state for the modern ocean. In this model, the global ocean is divided simply into a euphotic layer and a deep layer at a depth of 100 m. A thin layer on the sediment surface is considered as the box of the ‘scavenged layer’, where organic matter is decomposed during early diagenesis²². In Fig. 6, the black figures are observed or previously published values, as described below. Magenta figures are values calculated using the

174 following equations¹¹, which assumes a steady-state for each box:

$$175 \quad \Sigma F_{in} = \Sigma F_{out}$$

$$176 \quad \Sigma F_{in} \delta_{in} = \Sigma F_{out} \delta_{out}$$

177

178 where F_{in} and F_{out} represent an input and output flux for the box, and δ_{in} and δ_{out}

179 represent $\delta^{65}\text{Cu}$ values of F_{in} and F_{out} , respectively. Based on this work, the

180 depth-weighted averages of Cu concentration and $\delta^{65}\text{Cu}$ are 1.1 nmol kg^{-1} and 0.49‰ in

181 surface seawater and 2.5 nmol kg^{-1} and 0.60‰ in deep seawater, respectively. The

182 water mixing rate between the upper box and lower box is assumed to be $1.2 \times 10^{15} \text{ m}^3$

183 year^{-1} , which has been determined from ^{14}C data²³. We assumed that the main inputs of

184 dissolved Cu to the ocean are riverine and atmospheric inputs. The reported riverine

185 input of dissolved Cu to the ocean among four studies^{4, 8, 24, 25} was in the range of

186 $6\text{--}9 \times 10^8 \text{ mol year}^{-1}$, and the average value of $7.6 \times 10^8 \text{ mol year}^{-1}$ was applied to our

187 model. The removal rate of dissolved Cu from the ocean was estimated to be $\sim 4.0 \text{ nmol}$

188 $\text{kg}^{-1} \text{ year}^{-1}$ by using a vertical advection diffusion model^{4, 5}. By multiplying this value

189 by the total ocean volume ($1.35 \times 10^{21} \text{ kg}$), the scavenging flux of Cu in the ocean was

190 estimated to be $5.4 \times 10^9 \text{ mol year}^{-1}$. Riverine input $\delta^{65}\text{Cu}$ was determined in rivers

191 worldwide; the rivers account for approximately one-quarter of all riverine discharge to

192 the ocean⁸. The discharge-weighted average of 0.68‰ of these rivers was used in our

model. The $\delta^{65}\text{Cu}$ of atmospheric input was assumed to be 0‰ because $\delta^{65}\text{Cu}$ values are ~0‰ for rainwater, leachable fractions of marine aerosols¹¹, and loess¹⁷. It was assumed that the $\delta^{65}\text{Cu}$ of sinking particles (of mainly biogenic origin) from surface water was the same as the $\delta^{65}\text{Cu}$ of ambient surface seawater (i.e., 0.49‰), because isotopic fractionation during phytoplankton uptake and adsorption onto phytoplankton surface is expected to be insignificant, as described above. The $\delta^{65}\text{Cu}$ of the benthic flux from the scavenged layer to deep seawater was assumed to be the global average of 0.58‰. This value is the average of $\delta^{65}\text{Cu}$ in seawater samples nearest the bottom of the ocean. The unknown Cu fluxes that were calculated by this model are those of supply from the atmosphere, transport by sinking particles from the surface, preservation in sediments, and return from the scavenged layer to deep water. The unknown $\delta^{65}\text{Cu}$ values calculated by this model are those of the transporting flux by sinking particles in deep water and the preserved flux into sediments.

Discussion

From our data we infer that the $\delta^{65}\text{Cu}$ values in surface seawater are mainly controlled by supply from rivers, atmosphere, and deep seawater. Biological uptake does not cause significant isotopic fractionation of Cu in the open ocean. $\delta^{65}\text{Cu}$ values

211 in deep seawater are heavier than those in surface seawater and become heavier with the
212 age of deep seawater because of preferential scavenging for the light isotope (^{63}Cu).

213 Biological fractionation of Cu isotopes has not yet been sufficiently clarified in
214 the literature. There are only a few studies concerning isotopic fractionation of Cu by
215 phytoplankton. Laboratory experiments have shown that uptake by several diatoms
216 caused no significant fractionation or slight enrichment of the heavy Cu isotope (^{65}Cu)
217 when the initial Cu concentration was $\sim 200 \text{ nmol L}^{-1}$ (ref. 26). However, a geochemical
218 study in the Garonne River suggested that diatom species prefer the light Cu isotope
219 (^{63}Cu)²⁷. Thus, it is necessary to determine the $\delta^{65}\text{Cu}$ of natural phytoplankton in the
220 open ocean in future work.

221 We suggest that Fe-Mn oxides may be a major sink of Cu in the oxic ocean.
222 $\delta^{65}\text{Cu}$ values of Fe-Mn nodules are $0.33 \pm 0.23\text{‰}$ (ave \pm 2-sd, $n = 14$) in the Pacific,
223 $0.25 \pm 0.26\text{‰}$ ($n = 8$) in the Atlantic, and $0.31 \pm 0.23\text{‰}$ ($n = 31$) in the world ocean¹⁰; the
224 $\delta^{65}\text{Cu}$ values of Fe-Mn crusts are $0.54 \pm 0.07\text{‰}$ ($n = 8$) in the Pacific, $0.33 \pm 0.15\text{‰}$ ($n =$
225 8) in the Atlantic, and $0.44 \pm 0.23\text{‰}$ ($n = 16$) in the world ocean¹¹. Thus, $\delta^{65}\text{Cu}$ of Fe-Mn
226 crusts and nodules is lighter than that of dissolved Cu in the ocean. Furthermore, the
227 $\delta^{65}\text{Cu}$ of Fe-Mn crusts is significantly heavier in the Pacific than in the Atlantic ($p =$
228 0.01). These data are consistent with preferential scavenging of ^{63}Cu and gradual

229 accumulation of ^{65}Cu in seawater through the global ocean circulation. This view,
230 however, seems contrary to experimental results on adsorption of Cu isotopes on Fe
231 oxyhydroxides^{26, 28}, which indicate enrichment of the heavy Cu isotope onto oxide
232 surfaces in NaNO_3 solutions or mixtures of acidic drainage and river water. The
233 discrepancy may be caused by differences in conditions, such as pH, Cu concentration,
234 and organic ligands concentration, between experimental solutions and natural seawater.
235 Additionally, it was found that Cu is associated with Mn and not Fe in Fe-Mn crusts²⁹.
236 Isotopic fractionation between free Cu and organic ligand-bound Cu would also be
237 important for Cu isotopes in seawater, because Cu is mostly complexed with organic
238 ligands. In a laboratory experiment, humic acid preferentially complexes with the heavy
239 Cu isotope³⁰. Therefore, it is likely that the complexation of Cu with dissolved organic
240 ligands in seawater also causes mass fractionation of Cu, because the organic ligands
241 and humic acid most likely have the same functional groups. Furthermore, Cu is
242 contained not only in the Fe-Mn oxide fraction but also in the organic fraction of
243 sinking particles^{31, 32}. Thus, understanding isotopic fractionation during scavenging of
244 dissolved Cu from seawater is not straightforward. It was originally proposed in a
245 previous field study of rivers and oceans that there is equilibrium partitioning of
246 isotopes between heavy Cu bound to organic ligands in the dissolved phase and light Cu

247 adsorbed to particles⁸. This hypothesis is consistent with our explanation of light Cu
248 scavenging.

249 In the box model using both the Cu concentration and $\delta^{65}\text{Cu}$ (Fig. 6), we
250 constrained the transporting flux of Cu from surface to deep water by sinking particles
251 to be $3.4 \times 10^9 \text{ mol year}^{-1}$. The residence time for dissolved Cu in surface water (<100 m)
252 is ~9 years, which is consistent with previous estimates of 3.2–11.7 years^{5, 33}. The
253 calculated preservation flux of Cu into sediments is $1.7 \times 10^8 \text{ mol year}^{-1}$. The overall
254 residence time of Cu in the ocean is calculated by dividing the average concentration by
255 the preservation flux. Our estimate of the overall residence time of Cu is 2000 years,
256 which is within the range of literature values (1700–6400 years)^{4, 11}. The calculated
257 $\delta^{65}\text{Cu}$ of preserved Cu in sediments is +0.30‰, which is quite similar to the averages
258 reported for Fe-Mn oxides^{10, 11}.

259 We also constrained the atmospheric input of dissolved Cu to be $9.6 \times 10^8 \text{ mol}$
260 year^{-1} . Our model suggests that the present atmospheric input of Cu is comparable to
261 the riverine input. A significant correlation was found between Cu and ^{210}Pb in surface
262 seawater, implying a strong atmospheric supply of Cu because ^{210}Pb is a tracer for
263 atmospheric input⁴. These authors estimated both the atmospheric and riverine Cu input
264 to be $6.0 \times 10^8 \text{ mol year}^{-1}$, which is similar to our results. However, our value is

265 significantly larger than the natural atmospheric input previously estimated at 5.4×10^7
266 mol year^{-1} , which was obtained by multiplying the total dust flux by the mean crustal
267 Cu concentration and solubility¹¹.

268 Two possible explanations are given to rationalise this difference. First, it is
269 possible that the Cu concentration and solubility in marine aerosols would be different
270 from those in the continental crust. The enrichment factor of Cu relative to Al in marine
271 aerosols varies over a large range of 1–200 compared with the continental crust²⁵. The
272 solubility of Cu in aerosols has a wide range of 15–86%³⁴. It was suggested that the
273 enriched and soluble Cu in aerosols is from anthropogenic sources^{34, 35, 36}. However,
274 Maring et al. evaluated the source of Cu enrichment in aerosols near Enewetak in the
275 North Pacific, suggesting that atmospheric soluble Cu is from primary natural origins
276 and that soil organic matter enriched in Cu could be a significant source of soluble Cu³⁷.
277 If anthropogenic Cu has significantly affected atmospheric input as we estimated, then
278 the steady-state assumption is imperfect for the modern ocean, because anthropogenic
279 inputs would have substantially increased in the recent ~100 years, whereas the overall
280 oceanic residence time of Cu is approximately 1000 years. Second, other fluxes to open
281 ocean surface may be suggested. One possible flux is from the continental shelf
282 sediment, where a portion of Cu is derived from the reduction of primary terrigenous

283 metal oxides³⁸. The $\delta^{65}\text{Cu}$ value of this flux would also be close to the crustal value
284 (‰) and lighter than that of surface seawater. If these fluxes are included in our box
285 model, then our estimate of atmospheric input may decrease. As described above, some
286 uncertainties remain in our box model. Our results, however, confirm possibilities of
287 this new box model based on both concentration and isotopic composition of trace
288 metals.

289

290 **Methods**

291 **Seawater samples**

292 The South Indian and North Pacific seawater samples were collected during the
293 R/V *Hakuho-maru* voyages KH 09-4, KH 10-2, KH 11-7, and KH 12-4 using a clean
294 sampling system¹⁴. In a clean booth, seawater was filtered through a 0.2 μm cartridge
295 (Acro pak, Poll), acidified with HCl to pH 1.7–2.2, and stored in 2 L or 4 L LDPE
296 bottles (Nalge Nunc) or 6 L LDPE cubic bags (Lontainer, Sekisui Seikei), which were
297 pre-cleaned by overnight treatment with 4 M HCl followed by rinsing with deionised
298 water. The North Atlantic sample was a GEOTRACES reference material collected at
299 BATS during the US-GEOTRACES KN193-5 voyage of the R/V *Knorr*. The South
300 Atlantic sample was collected at Station 3 during the UK-GEOTRACES D357 voyage

301 of the RSS *Discovery*.

302

303 **Rainwater samples**

304 Rainwater was collected from two sites using pre-cleaned polyethylene funnels
305 and cubic bags (Lontainer) or 2 L LDPE bottles. One site was on the roof of the main
306 building of the Institute for Chemical Research, which is located in an urban area of the
307 Main Island, Japan. The other site was on top of Mt. Kajigamori, which is located in a
308 rural area of Sikoku Island. Rainwater samples were filtered through a 0.22 μm filter
309 (Millipore) and acidified with HCl to pH 1.7–2.1.

310

311 **Analytical procedure of $\delta^{65}\text{Cu}$ and Cu**

312 Copper concentration and isotopic composition were determined as described
313 in a previous paper¹². Briefly, Cu in seawater or rainwater was collected using a column
314 of Nobias chelate PA-1 resin (Hitachi High Technologies) followed by elution with 1 M
315 HNO_3 . The eluate was evaporated to dryness, and the residue was re-dissolved with 10
316 M HCl. The sample was passed through a column of anion exchange resin (AG MP-1,
317 Bio-Rad); additional 10 M HCl was then passed through the column to remove
318 co-existing elements, followed by the elution of Cu with 5 M HCl. This eluate was

evaporated to dryness and the residue was re-dissolved with 1 M HNO₃. Finally, the 1
M HNO₃ solution was re-evaporated and the residue was re-dissolved with 0.4 M HNO₃,
yielding the pre-concentrated sample. One hundred micrograms of the pre-concentrated
sample was diluted with 0.4 M HNO₃ by a factor of ~10 and used for measurement of
Cu concentration. Co-existing Na, Mg, Ba, Ni, Zn, Cr, and Ti were also measured to
ascertain whether these interfering elements possessed concentrations sufficiently low
to permit accurate Cu isotopic measurements. When the Na (ppb)/Cu (ppb) ratio in the
pre-concentrated sample was higher than 1, the solution was not used for discussion.
For the Cu isotopic measurement, which used a multicollector ICP-MS (Thermo
Finnigan Neptune or Neptune Plus), the final solution was diluted to adjust the Cu
concentration to 50 ppb and Zn was added to give a solution of 100 ppb for external
normalisation. The precision of this method was evaluated previously by repeated
analyses of coastal seawater to be $\pm 0.07\text{‰}$ ($\pm 2\text{-sd}$, $n = 6$)¹². In this study, 34 samples
were each divided into two aliquots and analysed in duplicate, resulting in an average
2-sd of 0.045 ‰ ($n = 34$) for $\delta^{65}\text{Cu}$ and 0.11 nmol kg⁻¹ ($n = 34$) for Cu concentration.
These values are shown as error bars in the figures.

References

- 337 1. Brand LE, Sunda WG & Guillard RRL. Reduction of marine phytoplankton
338 reproduction rates by copper and cadmium. *J. Exp. Biol. Ecol.* **96**, 225-250
339 (1986).
- 340
- 341 2. Coale KH & Bruland KW. Copper complexation in the Northeast Pacific.
342 *Limnol. Oceanogr.* **33**, 1084-1101 (1988).
- 343
- 344 3. Bruland KW & Lohan MC. Controls of Trace Metals in Seawater. In: *Treatise on*
345 *Geochemistry* (ed[^](eds Holland HD, Turekian KK). Elsevier (2003).
- 346
- 347 4. Boyle EA, Sclater FR & Edmond JM. The distribution of dissolved copper in the
348 Pacific. *Earth Planet. Sci. Lett.* **37**, 38-54 (1977).
- 349
- 350 5. Bruland KW. Oceanographic distributions of cadmium, zinc, nickel, and copper
351 in the North Pacific. *Earth Planet. Sci. Lett.* **47**, 176-198 (1980).
- 352
- 353 6. Boyle EA, *et al.* GEOTRACES IC1 (BATS) contamination-prone trace element
354 isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr.*

355 *Methods* **10**, 653-665 (2012).

356

357 7. Bermin J, Vance D, Archer C & Statham PJ. The determination of the isotopic
358 composition of Cu and Zn in seawater. *Chem. Geol.* **226**, 280-297 (2006).

359

360 8. Vance D, *et al.* The copper isotope geochemistry of rivers and the oceans. *Earth*
361 *Planet. Sci. Lett.* **274**, 204-213 (2008).

362

363 9. Thompson CM, Ellwood MJ & Wille M. A solvent extraction technique for the
364 isotopic measurement of dissolved copper in seawater. *Anal. Chim. Acta* **775**,
365 106-113 (2013).

366

367 10. Albarède F. The Stable Isotope Geochemistry of Copper and Zinc. In:
368 *Geochemistry of Non-Traditional Stable Isotopes* (ed[^](eds Johnson CM, Beard
369 BL, Albarède F). Mineralogical Society of America (2004).

370

371 11. Little SH, Vance D, Walker-Brown C & Landing WM. The oceanic mass
372 balance of copper and zinc isotopes, investigated by analysis of their inputs, and

- 373 outputs to ferromanganese oxide sediments. *Geochim. Cosmochim. Acta* **125**,
374 673-693 (2014).
- 375
- 376 12. Takano S, Tanimizu M, Hirata T & Sohrin Y. Determination of isotopic
377 composition of dissolved copper in seawater by multi-collector inductively
378 coupled plasma mass spectrometry after pre-concentration using an
379 ethylenediaminetriacetic acid chelating resin. *Anal. Chim. Acta* **784**, 33-41
380 (2013).
- 381
- 382 13. Schlitzer R. Ocean Data View. <http://www.awi-bremerhaven.de/GEO/ODV>
383 (2002).
- 384
- 385 14. Vu HTD & Sohrin Y. Diverse stoichiometry of dissolved trace metals in the
386 Indian Ocean. *Sci. Rep.* **3**, 1745 (2013).
- 387
- 388 15. Zhao Y, Vance D, Abouchami W & de Baar HJW. Biogeochemical cycling of
389 zinc and its isotopes in the Southern Ocean. *Geochim. Cosmochim. Acta* **125**,
390 653-672 (2014).

391

392 16. Lupton J. Hydrothermal helium plumes in the Pacific Ocean. *J. Geophys. Res.*
393 **103**, 15853-15868 (1998).

394

395 17. Li W, Jackson SE, Pearson NJ, Alard O & Chappell BW. The Cu isotopic
396 signature of granites from the Lachlan Fold Belt, SE Australia. *Chem. Geol.* **258**,
397 38-49 (2009).

398

399 18. Abouchami W, *et al.* Biogeochemical cycling of cadmium isotopes in the
400 Southern Ocean along the Zero Meridian. *Geochim. Cosmochim. Acta* **127**,
401 348-367 (2014).

402

403 19. Ripperger S, Rehkämper M, Porcelli D & Halliday AN. Cadmium isotope
404 fractionation in seawater — A signature of biological activity. *Earth Planet. Sci.*
405 *Lett.* **261**, 670-684 (2007).

406

407 20. Xue Z, *et al.* Cadmium isotope variations in the Southern Ocean. *Earth Planet.*
408 *Sci. Lett.* **382**, 161-172 (2013).

409

410 21. Abouchami W, *et al.* Modulation of the Southern Ocean cadmium isotope
411 signature by ocean circulation and primary productivity. *Earth Planet. Sci. Lett.*
412 **305**, 83-91 (2011).

413

414 22. Chester R, Thomas A, Lin FJ, Basaham AS & Jacinto G. The solid state
415 speciation of copper in surface water particulates and oceanic sediments. *Mar.*
416 *Chem.* **24**, 261-292 (1988).

417

418 23. Sarmiento JL. *Ocean Biogeochemical Dynamics*. Princeton University Press
419 (2006).

420

421 24. Gaillardet J, Viers J & Dupré B. 5.09 - Trace Elements in River Waters. In:
422 *Treatise on Geochemistry* (ed[^](eds Holland HD, Turekian KK). Elsevier (2003).

423

424 25. Chester R & Jickells T. *Marine Geochemistry*. Willey-Blackwell (2012).

425

426 26. Pokrovsky OS, Viers J, Emnova EE, Kompantseva EI & Freydier R. Copper

- 427 isotope fractionation during its interaction with soil and aquatic microorganisms
428 and metal oxy(hydr)oxides: Possible structural control. *Geochim. Cosmochim.*
429 *Acta* **72**, 1742-1757 (2008).
430
- 431 27. Petit JCJ, *et al.* Anthropogenic sources and biogeochemical reactivity of
432 particulate and dissolved Cu isotopes in the turbidity gradient of the Garonne
433 River (France). *Chem. Geol.* **359**, 125-135 (2013).
434
- 435 28. Balistrieri LS, Borrok DM, Wanty RB & Ridley WI. Fractionation of Cu and Zn
436 isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental
437 mixing of acid rock drainage and ambient river water. *Geochim. Cosmochim.*
438 *Acta* **72**, 311-328 (2008).
439
- 440 29. Little SH, Sherman DM, Vance D & Hein JR. Molecular controls on Cu and Zn
441 isotopic fractionation in Fe–Mn crusts. *Earth Planet. Sci. Lett.* **396**, 213-222
442 (2014).
443
- 444 30. Bigalke M, Weyer S & Wilcke W. Copper isotope fractionation during

445 complexation with insolubilized humic acid. *Environ. Sci. Technol.* **44**,
446 5496-5502 (2010).

447

448 31. Fischer K, Dymond J, Lyle M, Soutar A & Rau S. The benthic cycle of copper:
449 Evidence from sediment trap experiments in the eastern tropical North Pacific
450 Ocean. *Geochim. Cosmochim. Acta* **50**, 1535-1543 (1986).

451

452 32. Noriki S, Shiribiki T, Yokomizo H, Harada K & Tsunogai S. Copper and nickel
453 in settling particle collected with sediment trap in the western North Pacific.
454 *Geochem. J.* **31**, 373-382 (1997).

455

456 33. Helmert E & Schrems O. Wet deposition of metals to the tropical North and the
457 South Atlantic ocean. *Atmos. Environ.* **29**, 2475-2484 (1995).

458

459 34. Duce RA, *et al.* The atmospheric input of trace species to the world ocean.
460 *Global Biogeochem. Cycles* **5**, 193-259 (1991).

461

462 35. Arimoto R, Ray BJ, Duce RA, Hewitt AD, Boldi R & Hudson A. Concentrations,

463 sources, and fluxes of trace elements in the remote marine atmosphere of New
464 Zealand. *Journal of Geophysical Research: Atmospheres* **95**, 22389-22405
465 (1990).

466

467 36. Desboeufs KV, Sofikitis A, Losno R, Colin JL & Ausset P. Dissolution and
468 solubility of trace metals from natural and anthropogenic aerosol particulate
469 matter. *Chemosphere* **58**, 195-203 (2005).

470

471 37. Maring HB & Duce RA. The impact of atmospheric aerosols on trace metal
472 chemistry in open ocean surface seawater: 2. Copper. *J. Geophys. Res.* **94**,
473 1039-1045 (1989).

474

475 38. Boyle EA, Husted SS & Jones SP. On the distribution of copper, nickel, and
476 cadmium in the surface waters of the North Atlantic and North Pacific Ocean. *J.*
477 *Geophys. Res.* **86**, 8048-8066 (1981).

478

479

480 **Acknowledgements**

We would like to thank Susan Little, Corey Archer, and Derek Vance (ETH, Zurich) for performing intercalibration with us and providing the South Atlantic sample. We also thank the officers and crew of the R/V *Hakuho-Maru* for their assistance in obtaining samples and Shoji Imai (The University of Tokushima) for sampling rainwater at the top of Mt. Kajigamori. We are grateful to Takanori Nakano and Kichoel Shin (Research Institute for Humanity and Nature) for their help with the MC-ICP-MS measurements. This work was supported by funds from the Steel Industry Foundation for the Advancement of Environmental Protection Technology and by grants-in-aids from the Japanese Society for the Promotion of Science.

Author contributions

S.T. and Y.S. designed the research. S.T. determined the concentration of Cu and $\delta^{65}\text{Cu}$. M.T. contributed to measurements with MC-ICP-MS. T.H helped with the development of the analytical method and supplied the standard reference material of Cu (NIST SRM 976). All authors contributed to the interpretation of the data and preparation of the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Figure legends

Figure 1 Station locations. Samples for the analysis of $\delta^{65}\text{Cu}$ were collected at these stations during R/V *Hakuho-maru* voyages. The numbers of samples are 10 at TR7, 10 at TR15, 10 at CR27, 14 at BD17, 12 at BD21, and 18 at ER10. This figure was produced with Ocean Data View¹³.

Figure 2 Representative vertical profiles of the concentration and isotopic composition of Cu. Magenta triangles indicate Cu concentration. Blue squares and black circles indicate $\delta^{65}\text{Cu}$ and apparent oxygen utilisation (AOU), respectively. Black diamonds indicate fluorescence or chlorophyll a (Chl. a). The error bars are 2-sd of $\pm 0.045\text{‰}$ for $\delta^{65}\text{Cu}$ and $\pm 0.11 \text{ nmol kg}^{-1}$ for Cu concentration, as described in the Methods section. The vertical profiles at all stations are shown in Supplementary Fig. 1.

Figure 3 $\delta^{65}\text{Cu}$ versus reciprocal Cu concentration for surface seawater (<100 m). The error bars of the magenta circles are 2-sd of $\pm 0.045\text{‰}$. The blue, black, and orange

shaded areas indicate the ranges of the data for deep seawater, river water, and rural rain, respectively. The magenta triangle indicates the possible range of mixtures of average deep seawater, river water, and rainwater. The surface water data shifted to the right of the triangle indicate that other processes decrease the dissolved Cu concentration in the surface seawater.

523

Figure 4 $\delta^{65}\text{Cu}$ versus AOU for seawater. The error bars for $\delta^{65}\text{Cu}$ are 2-sd of $\pm 0.045\%$.

(a) All $\delta^{65}\text{Cu}$ values were plotted against AOU. The solid line was determined by a regression analysis of all plots: $\delta^{65}\text{Cu} = 0.00067 \times \text{AOU} + 0.50$, $R^2 = 0.60$, $n = 77$, $p < 0.001$. (b) $\delta^{65}\text{Cu}$ values were plotted against AOU in deep seawater (>2000 m). The solid line was determined by a regression analysis of all plots: $\delta^{65}\text{Cu} = 0.0016 \times \text{AOU} + 0.32$, $R^2 = 0.70$, $n = 25$, $p < 0.001$.

530

Figure 5 Cu concentration versus AOU in the ocean. The error bars are 2-sd of ± 0.11 nmol kg^{-1} . The solid line was defined as: $[\text{Cu}] = 0.0046 \times \text{AOU} + 1.5$, $R^2 = 0.31$, $n = 77$, $p < 0.001$.

534

535 Figure 6 Box model for Cu cycling in the ocean based on both elemental concentration
536 and isotopic ratio. The Roman and italic values below the process names represent Cu
537 flux in units of $10^9 \text{ mol year}^{-1}$ and $\delta^{65}\text{Cu}$ values, respectively. Black figures indicate
538 observed values and magenta figures indicate values calculated based on mass balance.

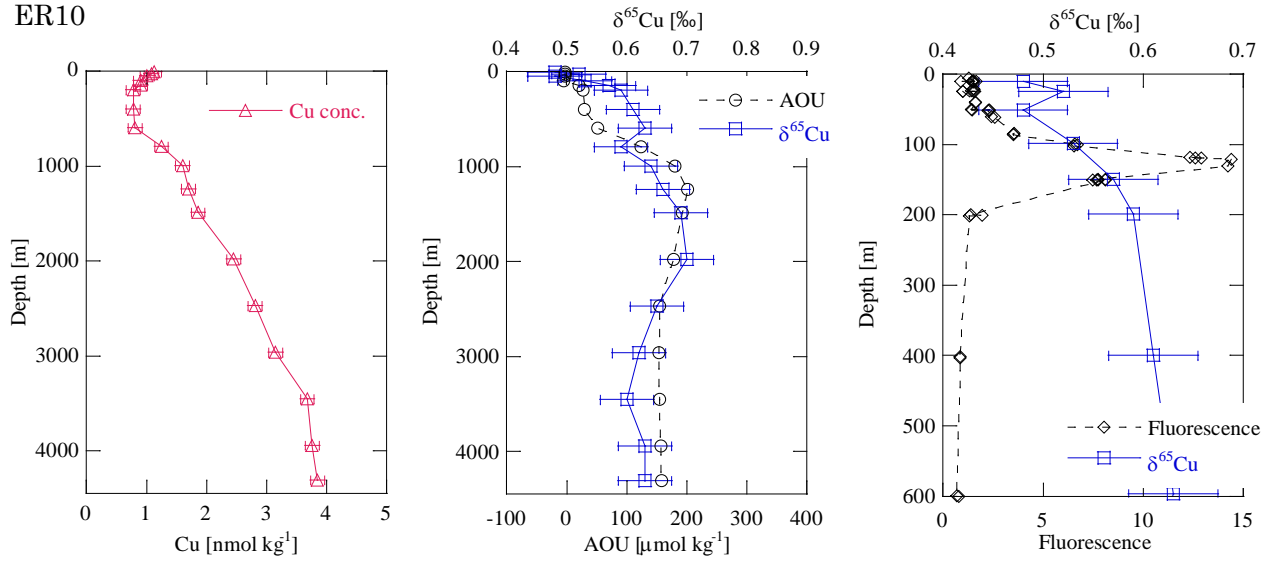
Table

Table 1 Rainwater analysis results

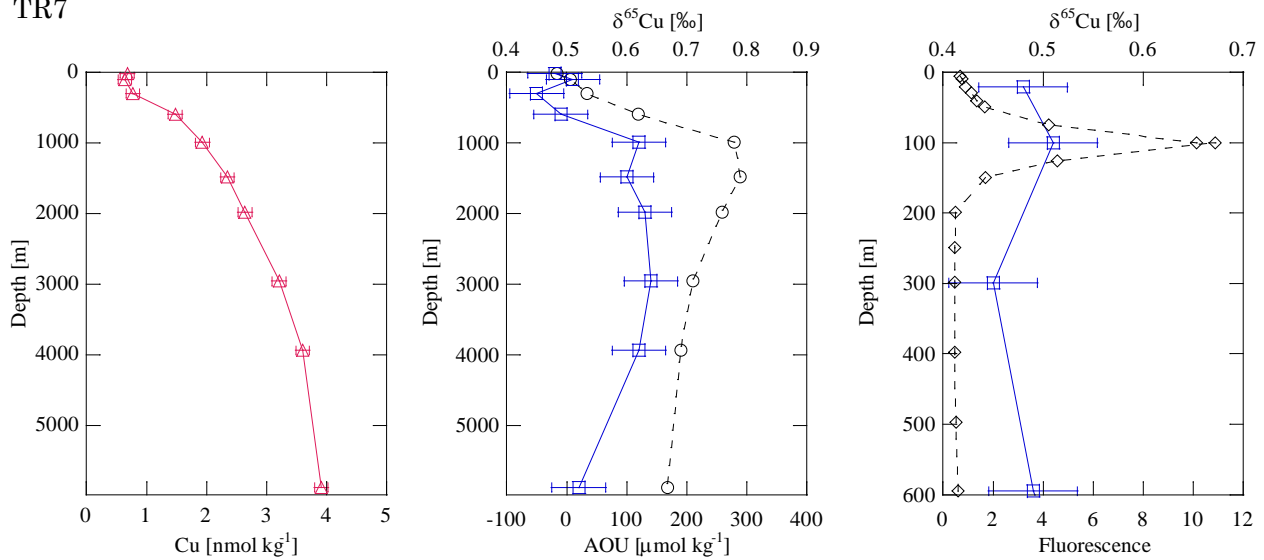
Sample ^a	Date	Cu [nmol kg ⁻¹]	δ ⁶⁵ Cu
Urban-1	3 Jul 2013	23.46	−0.12
Urban-2	20 Jun 2013	1.51	−0.08
Urban-3	26 Jun 2013	1.84	0.03
Rural-1	16 Jun 2013	1.12	−0.03
Rural-1	16 Jun 2013	1.14	−0.01
Rural-2	8 Jul 2013	2.60	0.03

^a ‘Urban’ samples were collected on the roof of the main building on the Uji campus on Main Island, Japan. ‘Rural’ samples were collected at the top of Mt. Kajigamori on Sikoku Island, Japan.

ER10

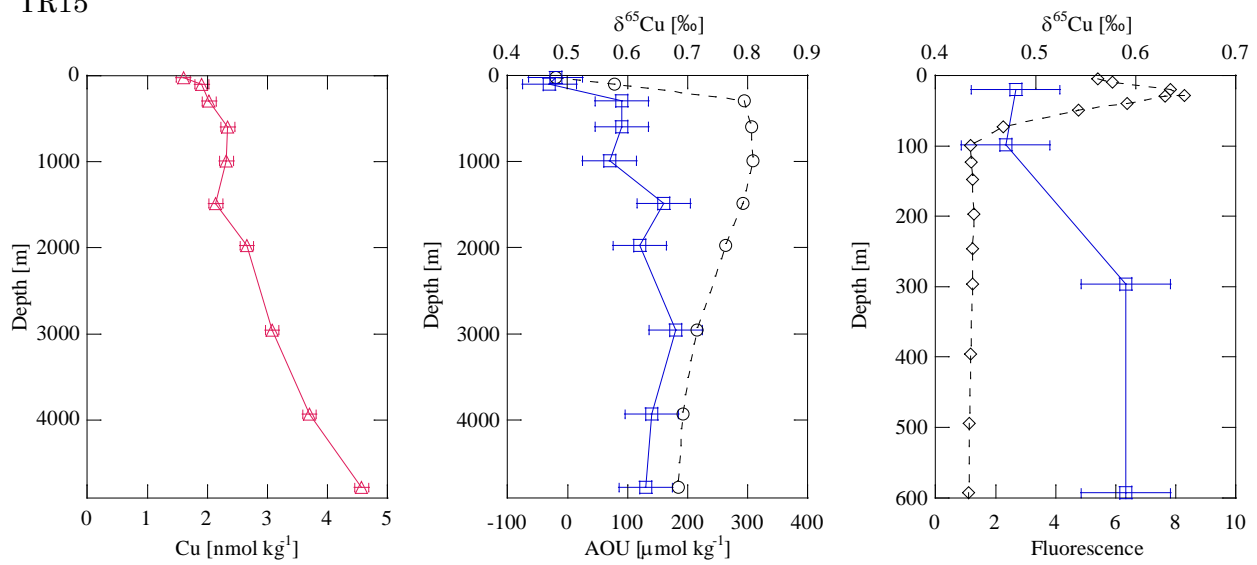


TR7

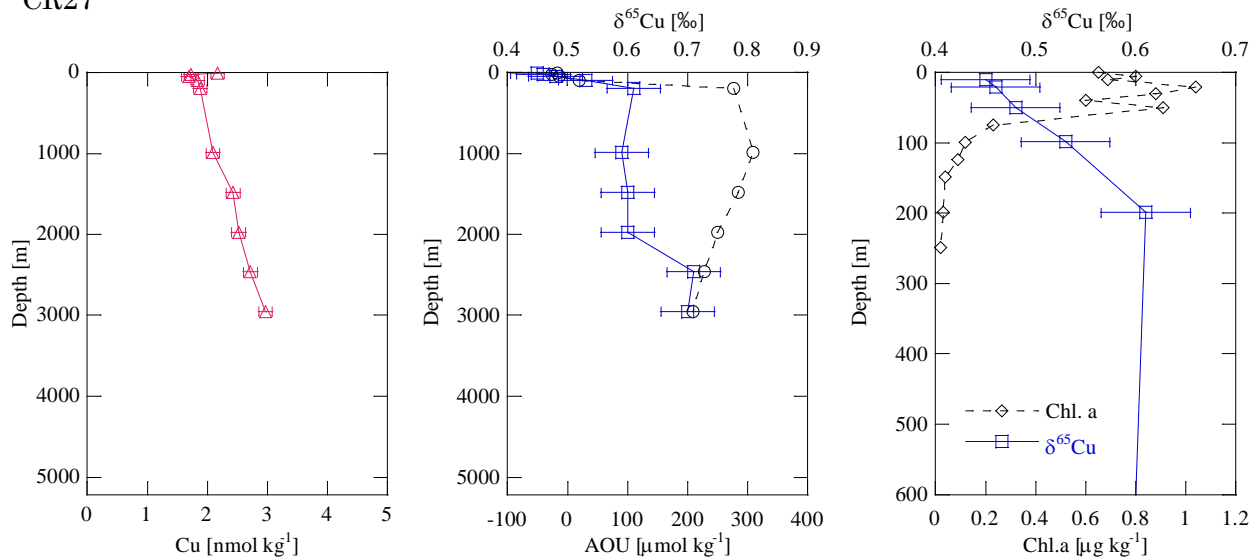


Supplementary Figure 1 Vertical profiles of Cu concentration, $\delta^{65}\text{Cu}$, apparent oxygen utilisation (AOU), and fluorescence or chlorophyll a (Chl. a) in the ocean. Magenta triangles indicate Cu concentration. Blue squares and black circles indicate $\delta^{65}\text{Cu}$ and AOU, respectively. Black diamonds indicate Chl. a or fluorescence.

TR15

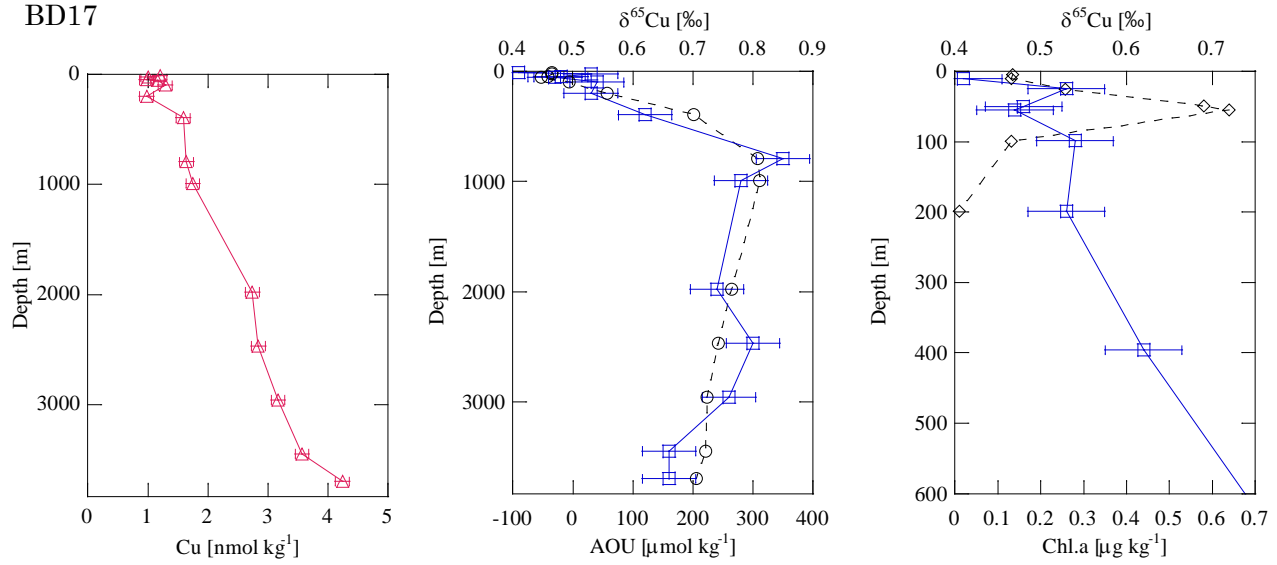


CR27

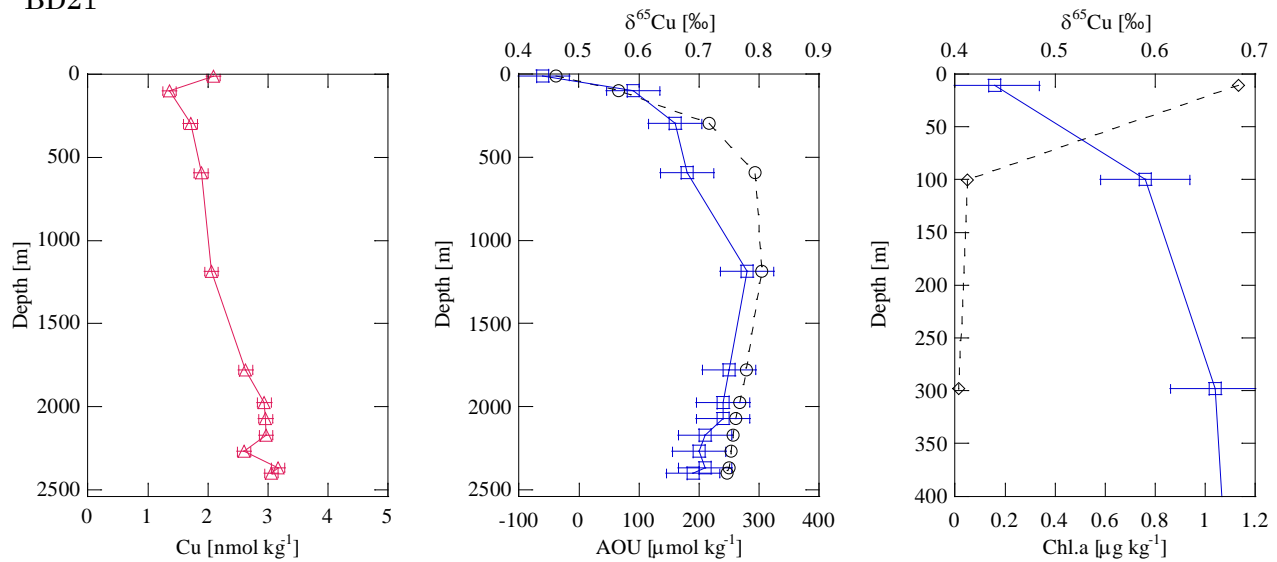


Supplementary Figure 1 (continued)

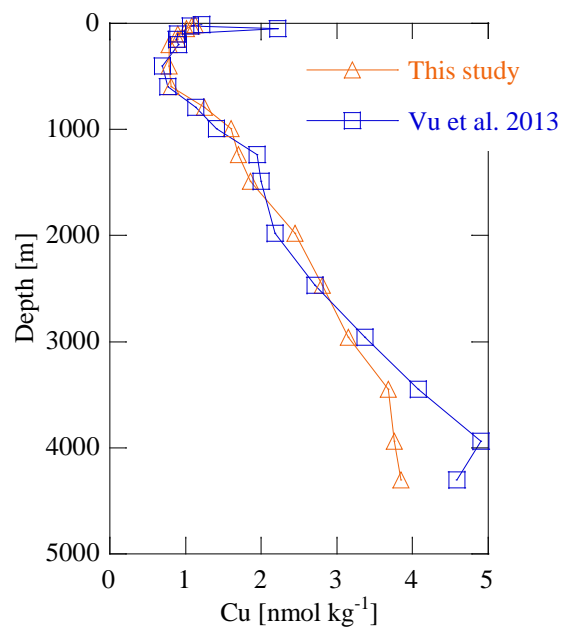
BD17



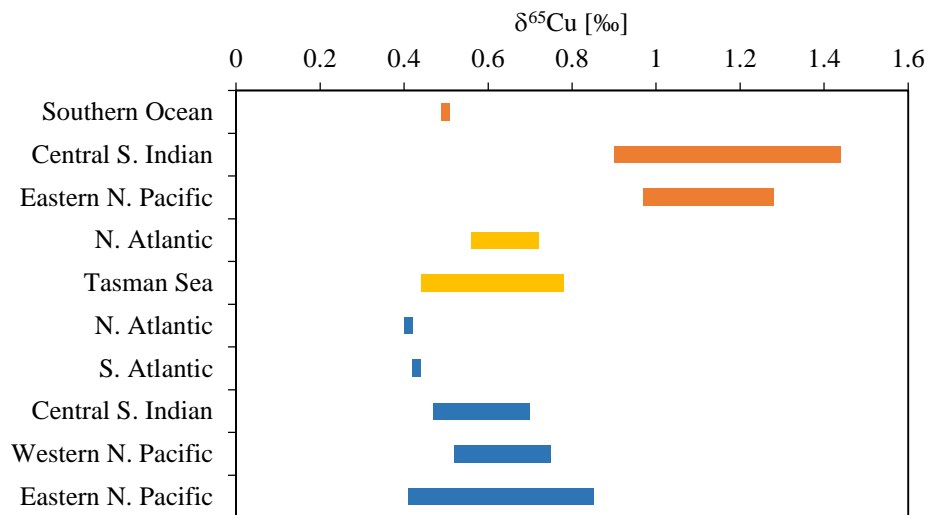
BD21



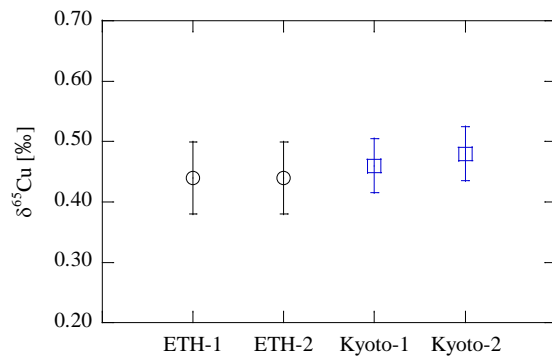
Supplementary Figure 1 (continued)



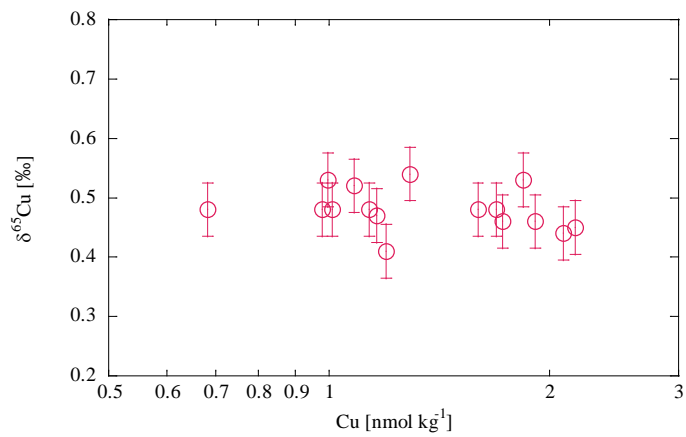
Supplementary Figure 2 Comparison of Cu concentration profiles at ER10 from a previous paper¹ and from this work. Blue squares and orange triangles represent data in the previous and present study, respectively.



Supplementary Figure 3 Comparison of dissolved $\delta^{65}\text{Cu}$ ranges in seawater. Orange and yellow bars indicate the ranges reported by British (ETH at present)^{2, 3} and Australian groups^{4, 5}, respectively. Blue bars indicate those in this study.



Supplementary Figure 4 Intercalibration of $\delta^{65}\text{Cu}$ in seawater between the method of the ETH group (black circles) and our method (blue squares). Uncertainties for the ETH methodology are based on repeated ($n = 29$) analyses of a secondary Cu standard over a period of 6 months. The seawater sample collected at a 7145 m depth near the Japan Trench was divided into 4 aliquots and analysed in duplicate with each method. The results were found to be consistent within uncertainties.



Supplementary Figure 5 The correlation between $\delta^{65}\text{Cu}$ and Cu concentration in the surface seawater (<100 m). Note that the horizontal axis is a logarithmic scale.

Supplementary Table 1 Seawater analysis results.

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]
<i>KH 11-7, TR7, 29.99N, 165.01E, depth 5883 m, 19 June 2011</i>								
21	0.48	0.68			0.48	0.68		
100	0.49	0.63	0.53	0.66	0.51	0.64	0.05	0.04
299	0.48	0.77	0.43	0.77	0.45	0.77	0.07	0.00
595	0.48	1.47	0.51	1.50	0.49	1.48	0.03	0.05
991	0.67	1.94	0.58	1.92	0.62	1.93	0.12	0.02
1484	0.60	2.35			0.60	2.35		
1979	0.63	2.68	0.62	2.59	0.63	2.64	0.02	0.12
2958	0.67	3.19	0.61	3.22	0.64	3.21	0.09	0.05
3938	0.62	3.66	0.61	3.54	0.62	3.60	0.01	0.18
5882	0.54	3.95	0.50	3.87	0.52	3.91	0.06	0.11
<i>KH11-7, TR15, 165.01°E, 51.00°N, depth 4802 m, 27 June 2011</i>								
20	0.46	1.59	0.50	1.61	0.48	1.60	0.06	0.03
99	0.46	1.90	0.46	1.93	0.46	1.91	0.00	0.04
296	0.61	2.03			0.61	2.03		
593	0.62	2.24	0.60	2.43	0.61	2.34	0.03	0.27
989	0.62	2.27	0.54	2.37	0.58	2.32	0.11	0.15
1482	0.70	2.25	0.62	2.02	0.66	2.14	0.12	0.32
1974	0.62	2.67			0.62	2.67		
2953	0.70	3.06	0.69	3.11	0.70	3.08	0.02	0.07
3929	0.65	3.51	0.67	3.90	0.66	3.70	0.04	0.54
4781	0.62	4.31	0.64	4.83	0.63	4.57	0.03	0.74
<i>KH11-7, TR17, 143.87°E, 37.81°N, depth 7150 m, 30 June 2011</i>								
7145	0.49	4.22	0.46	4.20	0.48	4.21	0.04	0.03

Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]	$\delta^{65}\text{Cu}$ [‰]	Cu [nmol kg ⁻¹]
<i>KH-10-2, CR27, 159.99°E, 46.97°N, depth 5114 m, 29 June 2010</i>								
10	0.46	2.21	0.45	2.13	0.45	2.17	0.00	0.11
21	0.45	1.78	0.47	1.68	0.46	1.73	0.03	0.15
50	0.46	1.71	0.50	1.68	0.48	1.69	0.05	0.04
99	0.52	1.92	0.54	1.77	0.53	1.84	0.04	0.21
199	0.63	1.90	0.59	1.87	0.61	1.88	0.05	0.05
990	0.60	2.10	0.58	2.09	0.59	2.09	0.03	0.02
1483	0.62	2.41	0.58	2.46	0.60	2.43	0.06	0.07
1974	0.60	2.57	0.60	2.48	0.60	2.52	0.01	0.12
2464	0.70	2.72	0.71	2.72	0.71	2.72	0.01	0.01
2954	0.72	2.99	0.68	2.95	0.70	2.97	0.07	0.06
<i>KH-12-4, BD17, 132.40°W, 43.00°N, depth 3732 m, 27–28 September 2012</i>								
11	0.41	1.20			0.41	1.20		
25	0.53	1.00			0.53	1.00		
50	0.48	0.98			0.48	0.98		
55	0.47	1.16			0.47	1.16		
99	0.54	1.29			0.54	1.29		
199	0.53	0.98			0.53	0.98		
396	0.62	1.59			0.62	1.59		
792	0.85	1.64			0.85	1.64		
989	0.78	1.75			0.78	1.75		
1975	0.74	2.74			0.74	2.74		
2466	0.80	2.84			0.80	2.84		
2956	0.76	3.17			0.76	3.17		
3445	0.66	3.57			0.66	3.57		
3695	0.66	4.24			0.66	4.24		

Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu
	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]
<i>KH-12-4, BD21, 128.43°W, 48.45°N, depth 2438 m, 30 September–1 October</i>								
11	0.44	2.09			0.44	2.09		
100	0.59	1.36			0.59	1.36		
298	0.66	1.71			0.66	1.71		
594	0.68	1.89			0.68	1.89		
1186	0.78	2.06			0.78	2.06		
1777	0.75	2.63			0.75	2.63		
1974	0.74	2.94			0.74	2.94		
2071	0.74	2.96			0.74	2.96		
2170	0.71	2.97			0.71	2.97		
2268	0.70	2.60			0.70	2.60		
2366	0.71	3.17			0.71	3.17		
2399	0.69	3.06			0.69	3.06		

Supplementary Table 1 (continued)

Depth [m]	First analysis		Second analysis		Average		2 s.d.	
	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu	$\delta^{65}\text{Cu}$	Cu
	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]	[‰]	[nmol kg ⁻¹]
<i>KH-09-5, ER10, 72.55°E, 20.00°S, depth 4343 m, 11 December 2009</i>								
11	0.48	1.13	0.48	1.14	0.48	1.13	0.01	0.02
25	0.51	1.07	0.52	1.09	0.52	1.08	0.02	0.03
51	0.50	1.01	0.46	1.01	0.48	1.01	0.05	0.01
99	0.50	0.90	0.55	0.90	0.53	0.90	0.07	0.01
150	0.58	0.90	0.55	0.89	0.57	0.90	0.05	0.01
199	0.61	0.79	0.57	0.77	0.59	0.78	0.06	0.02
400	0.61	0.78			0.61	0.78		
597	0.63	0.81			0.63	0.81		
795	0.59	1.25			0.59	1.25		
993	0.64	1.60			0.64	1.60		
1240	0.66	1.70			0.66	1.70		
1486	0.69	1.86			0.69	1.86		
1979	0.70	2.45			0.70	2.45		
2470	0.65	2.81			0.65	2.81		
2962	0.62	3.15			0.62	3.15		
3452	0.60	3.68			0.60	3.68		
3941	0.63	3.76			0.63	3.76		
4306	0.63	3.85			0.63	3.85		
<i>BATS, 64.10°E, 31.40°N, depth 4500 m</i>								
2000	0.41	1.70			0.41	1.59		
<i>D357, #163, 13.39°E, 36.46°S, depth 4894 m</i>								
4723	0.44	2.87	0.42	2.89	0.43	2.88	0.03	0.01
Average					0.60	2.20	0.045	0.11
<i>n</i>					77	77	34	34

Supplementary Table 2 Box model for Cu cycling in the ocean^a

			$\delta^{65}\text{Cu}$	Cu flux [10^9 mol y^{-1}]
Surface seawater	Input	Atmospheric	0.00	0.96
		Riverine	0.68	0.76
		Upwelling	0.60	3.0
$[\text{Cu}] = 1.1 \text{ nmol kg}^{-1}$ $\delta^{65}\text{Cu} = 0.49$	Output	Downwelling	0.49	1.3
		Particulate	0.49	3.4
Deep seawater	Input	Downwelling	0.49	1.3
		Benthic	0.58	3.7
		Particulate	0.49	3.4
$[\text{Cu}] = 2.5 \text{ nmol kg}^{-1}$ $\delta^{65}\text{Cu} = 0.60$	Output	Upwelling	0.60	3.0
		Particulate	0.49	5.4
Scavenged Layer	Input	Particulate	0.49	5.4
		Benthic	0.58	3.7
		Preserved	0.30	1.7

^a Black and magenta figures are the observed and calculated values, respectively.

Supplementary Methods

Intercalibration of seawater $\delta^{65}\text{Cu}$

We performed the intercalibration of $\delta^{65}\text{Cu}$ with the ETH group using a seawater sample collected at a depth of 7145 m near the Japan Trench (TR17, 143.87°E, 37.81°N, bottom depth 7150 m). This sample was divided into 4 aliquots and analysed twice with both the methodology of the ETH group and our method. The obtained $\delta^{65}\text{Cu}$ values were consistent between the ETH group and us, as shown in Supplementary Fig. 4.

The ETH group pre-concentrated Cu from seawater using a co-precipitation technique with $\text{Al}(\text{OH})_3$. The detail of this technique is described in Zhao et al. (2014)⁶. The pre-concentrated metal fraction was purified twice using anion exchange chromatography, as described in Archer and Vance (2004)⁷. The purified sample was oxidised by refluxing in $\text{HNO}_3 + \text{H}_2\text{O}_2$ (ref. 8). After evaporating the sample to dryness, the residue was re-dissolved with 2% nitric acid for isotopic measurements on a multi-collector ICP-MS. The setting of the multi-collector ICP-MS is detailed in Little et al. (2014)⁸.

Supplementary References

1. Vu HTD & Sohrin Y. Diverse stoichiometry of dissolved trace metals in the Indian Ocean. *Sci. Rep.* **3**, 1745 (2013).
2. Bermin J, Vance D, Archer C & Statham PJ. The determination of the isotopic composition of Cu and Zn in seawater. *Chem. Geol.* **226**, 280-297 (2006).
3. Vance D, *et al.* The copper isotope geochemistry of rivers and the oceans. *Earth Planet. Sci. Lett.* **274**, 204-213 (2008).
4. Boyle EA, *et al.* GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. *Limnol. Oceanogr, Methods* **10**, 653-665 (2012).
5. Thompson CM, Ellwood MJ & Wille M. A solvent extraction technique for the isotopic measurement of dissolved copper in seawater. *Anal. Chim. Acta* **775**, 106-113 (2013).
6. Zhao Y, Vance D, Abouchami W & de Baar HJW. Biogeochemical cycling of zinc and its isotopes in the Southern Ocean. *Geochim. Cosmochim. Acta* **125**, 653-672 (2014).

7. Archer C & Vance D. Mass discrimination correction in multiple-collector plasma source mass spectrometry: An example using Cu and Zn isotopes. *J. Anal. At. Spectrom.* **19**, 656-665 (2004).

8. Little SH, Vance D, Walker-Brown C & Landing WM. The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments. *Geochim. Cosmochim. Acta* **125**, 673-693 (2014).